

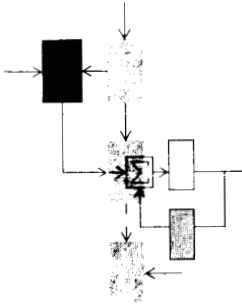
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AN ELECTRON MICROSCOPIC INVESTIGATION OF CdS THIN-FILM SURFACES

Anthony A. Aponick

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Electronic Systems Laboratory

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS

Department of Electrical Engineering

AN ELECTRON MICROSCOPIC INVESTIGATION
OF CdS THIN-FILM SURFACES

by

Anthony A. Aponick

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Electronic Systems Laboratory
Department of Electrical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

ABSTRACT

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The vacuum-deposited CdS thin-film surface is studied in detail by especially developed electron microscope techniques. The structure of the surface is found to vary with substrate temperature and deposition rate.

The surface is then coated with small amounts of gold at various deposition substrate temperatures, and found to present an extremely uniform and high density distribution of active nucleation sites.

Thermal treatments are described which prevent these nucleation sites from forming a completely continuous gold film at high surface mass densities.

Author

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I. INTRODUCTION

This report describes an investigation of the surface structure of evaporated CdS thin films and shows how variations in the deposition process affect this structure. The surface is also studied as a substrate for gold depositions under varying conditions. The results are applicable to device work in two ways: first, as a study of the structural nature of a thin film electrical contact; second, as an investigation of the possibility that a "grid-like" structure can be formed with gold on CdS for use in field-effect devices.

The study was begun with a survey of the relative merits of the various electron microscopic techniques currently in use. Carbon replication was chosen for use in this investigation because of its high-resolution capability and its elimination of the specimen damage inherent in any direct observation technique. A process for evaporating the carbon replicas was developed in which the contacts to the carbon source material were able to withstand the extremely high temperatures necessary for a slow, continuous evaporation. It was found that with this process the resolution of the replicas approached 30 \AA with no specimen damage, which represents a great improvement over the somewhat faster standard technique of "pulsed" evaporation.

When this technique was applied to CdS thin films evaporated from a Molybdenum boat, the surface structure was found to have a strong dependence on the deposition substrate temperature. With the substrate at room temperature, the deposition proceeds at a uniformly high rate of $400\text{-}500 \text{ \AA}/\text{min}$ and the resultant CdS surface consists of extremely fine grains which exhibit no apparent crystallinity. At elevated substrate temperatures, however, the deposition starts at a high and uniform rate, then begins to decay as the source is exhausted of its material. This exhaustion occurs for two reasons: First, at very high temperatures, the initial condensation rate is suppressed, probably due to re-evaporation from the substrate; and second, it was discovered that there is a lag from the time that the source is brought up to evaporation temperature until the time that the first visible condensation occurs. This lag time is directly dependent on the substrate temperature, but is otherwise not well understood. In either case, it is seen that a source must evaporate more material to reach a given thickness on a hot substrate than it would to reach the same thickness on a substrate at room temperature.

The surfaces of samples deposited at these substrate temperature are crystalline, and show increasing grain size with increasing temperature. An explanation for this effect is proposed in an argument that the reduced deposition rates, after the source becomes exhausted, enable the still mobile, freshly deposited material more time to come to a crystalline equilibrium with the previously condensed material on the substrate. The more time a mobile molecule has before becoming trapped by other mobile molecules, the more likely it is that it will be able to orient itself with the surface beneath, increasing the crystalline grain size of that surface.

These surfaces were then coated with very small amounts of gold at various substrate temperatures, and a careful study was made of the resultant gold structures. It was found that the extremely small spherical nuclei deposited on the surface at room temperature can be made to coalesce into larger agglomerates of these nuclei by heating the substrate either during or after deposition. A post-deposition heat treatment had a much more pronounced effect than an elevated deposition substrate temperature. It is argued that the amount of coalescence which occurs is a function of the magnitude of the adhesive force between the gold and the CdS surface. The strength of this adhesion, then, is a function of temperature, and was also found to be weaker on the surfaces grown at lower deposition rates. These arguments were checked and found to be supported at surface mass densities of gold up to $8.23 \mu\text{g}/\text{cm}^2$. Grain sizes of up to 300 \AA separated by an average distance of up to 100 \AA have been produced. This represents a considerable advance (over the continuous "solid layers" formed on the CdS surface at room temperatures) in the search for a fabrication method for grid-like structures.

A diffraction analysis was performed on the material near the surface of the CdS deposits. No direction of preferred orientation was detected for films of the thickness used in this work.

An unusual structure of distinctly hexagonal symmetry was discovered and often recorded for these CdS surface specimens. The structure was carefully measured and found not to agree with any published data for crystals of composition appropriate to this work. It is believed that the structure is a form of CdO (usually cubic) peculiar to oxidized CdS films deficient in sulfur and to Cd films which are oxidized on the substrate.

II. TECHNIQUES OF THE INVESTIGATION

A. SAMPLE FABRICATION

All samples for this investigation were made in a CEC LC 1-18A vacuum coating unit using a source-to-substrate distance of 9.5 inches and a standard pressure of $1-2 \times 10^{-5}$ Torr.

The substrates were ordinary Fisher glass microscope slides, cleaned by ultra-sonic vibration in detergent, rinsed in distilled water, then isopropanol, and heat dried in isopropanol vapor.

The CdS used was Baker and Adamson "Purified CdS", Lot P042. No refining techniques were used.

When the substrate was heated, a General Electric 250 watt quartz rod heater was mounted 3 cm. above the slide, running along a diagonal of the slide. Temperatures were measured on the back (uncoated) side of the substrate with a firmly clamped Iron-Constantan thermocouple, referenced to an ice bath and read with a Leeds and Northrup Potentiometer. Substrates were equilibrated thermally for at least one hour before deposition.

The sources for the evaporation were molybdenum boats. Source temperatures in the working range were calibrated against the current in the power supply transformer primary by making pyrometer measurements on an empty boat through the clean, evacuated bell jar. The same sources and temperature calibration procedures were used for the gold nucleation study, in which all depositions were done at a source temperature of 1300°C .

Before actually evaporating any CdS, the source was heated to about 800°C for 10 minutes to "degas" the material, as well as to fuse it into a cake which would not bounce out of the boat during evaporation. All depositions were done at a standard source temperature of 885°C .

The thickness of the CdS deposit was monitored using the colors of the interference fringes it produces in reflected incandescent light. The wavelengths of these colors were determined by subjectively comparing them with those produced by a set of Bausch and Lomb interference filters. All CdS depositions were made to a standard finished thickness of 2625 \AA . The surface mass densities of the gold deposits were obtained by evaporating a known mass of material and calculating the density from the Knudsen surface source law.

Parameters were measured at 30-to-60-second intervals as determined by a stopwatch, and were thus obtained as functions of time.

B. PREPARATION FOR MICROSCOPY

Since the primary concern of the investigation is the observation of physical structure as found under conditions approaching as nearly as possible those found in samples made for electrical measurements, it was desired to examine the sample thoroughly, yet minimize the damage incurred in specimen preparation.

These considerations eliminate the possibility of using two of the simpler direct transmission techniques:

1. The film can be stripped off the substrate, and placed on an electron microscope grid, and observed directly. Since stripping damage, due to strong local adhesions to the substrate or to strains set up in the film during handling can be very severe, this method is inadequate even if a thin support film is stretched over the microscope grid.
2. It is possible to coat a grid with a thin support film of SiO_2 , which presumably approximates the surface of a glass substrate. This grid could then be mounted on a slide, coated, and removed with no specimen damage whatever, but it was found that a working thickness of CdS (about 2,600 Å) is completely opaque to the electron beam, and that the presence of the grid on the slide during evaporation, due to its different thermal conductivity, sets up an extremely uneven thermal distribution over the face of the substrate. The CdS will selectively deposit everywhere but on the grid.

The method finally selected for use was replication, a process which consists of simply making a cast of the surface with some suitable fine-grain material, then "shadowing" the replica with some dense (high electron scattering power) metal. "Shadowing" is evaporating this metal onto the replica at an angle sufficient to show the surface features of the sample as gradations in thickness of the resultant deposit. This technique has the additional advantage that heights or depths of surface asperity can be inferred from the lengths of the shadows.

Considerations which enter into the choice of a suitable replicating material are that the material must not damage or chemically react with the sample, and that it should be fine-grained enough to fill all the crevices in the sample (i.e., have a high resolution). Also, it must be possible to remove the replica from the sample without damage.

One such material which was thoroughly investigated and later found inadequate was Parlodion dissolved in N-Butyl Acetate (or Formvar in dioxane). This solution is dropped onto the sample, the Acetate evaporates, and the result is a plastic cast of the surface which can be easily separated and placed on a grid. Although the method is capable of sufficient resolution for this work, it was found that the slightest increase in temperature (as upon exposure to the electron beam) will melt all of the high-resolution parts of the replica, leaving only the replication of gross structure of characteristic size 500 \AA or larger. In addition, there is the possibility that the physical contact of the solution may damage the sample.

This material was finally abandoned in favor of evaporated carbon. The sample is placed 12 cm. above a 5 cm. length of 3 mm. carbon rod of the quality used for spectroscopy. The last 2.5 mm. of this rod is turned down to a 1.5 mm. diameter, and the rod, spring loaded at the thick end, is forced up against a 1 cm. block of spectroscopic carbon. Electrical contact is made to the thin carbon rod through a tantalum collar, placed 4-5 mm. from the turned-down end, and to the large carbon block through its holder. High currents traversing this path heat the turned-down segment of carbon to temperatures sufficient to evaporate the carbon with no damage to the holders, spring, or contact electrodes. Eight such rods are used on each sample. If care is exercised, no arcing occurs, and the sample becomes coated with about 300 \AA of extremely fine-grain carbon. The temperature rise of the sample is less than 40°C due to its large distance from the source. Although this method is extremely time consuming when compared with the standard carbon method where the sample is placed only 4 cm. from the electrodes, and all of the carbon replica is evaporated at once with a high-current pulse, it was found by experiment that any less patient method is useless. The loss of resolution and sample damage caused by standard methods make the replica inadequate for the high-magnification investigations of this work.

The resolution of these replicas have been found to be so high that they are nearly impossible to strip from the sample. This problem is circumvented by dissolving the CdS in HCl. Fortunately, HCl is the best solvent for CdS of all the ordinary acids, and it has the least effect on the carbon. HNO_3 and H_2SO_4 tend to wrinkle the carbon replica. The method for dissolving the CdS consists of slowly immersing the slide into the HCl so that the surface tension of the solution lifts up the replica as it dissolves the CdS. When the stripping

operation is finished, the replica is floating on the surface of the solution. The replica is washed in a buffer and then in distilled water. These washes are accomplished by gently picking up the replica on a clean slide and floating it off onto the various baths. The replica is then broken into segments which are mounted on grids for shadowing and examination under the microscope. All shadow casting for the specimens of this investigation was done at an angle of 60° and a surface mass density of chromium of approximately $3 \mu\text{g}/\text{cm}^2$. This was found to be the optimum procedure with respect to contrast, resolution, and chromium grain size.

This material is capable of resolutions better than 30 \AA when the above method of depositing the carbon is used. The replicas are insensitive to electron beam heating if they are kept dry by storing under vacuum until examination. ("Wet" replicas, not stored under vacuum, flex, break, and jitter under the electron beam). The damage incurred by the sample in this process is slight and very noticeable where it occurs. (See Figs. 1 and 2).

This method carries with it the additional advantage that nucleated gold remains stuck in the replica and can be directly examined, leaving no uncertainty as to the spacings of size of the nuclei. If such a "combination" replica is shadowed, the location of nuclei with respect to the CdS surface can be seen, and where gold has not remained stuck in the replica, the height of the nuclei may be inferred from shadow length. Electron diffraction analyses may be performed on such residual gold, as well as on any CdS which may not have been dissolved.



Fig. 1 Parlodion replica shadowed with Cr. Note general lack of fine resolution.
(80,000 x)

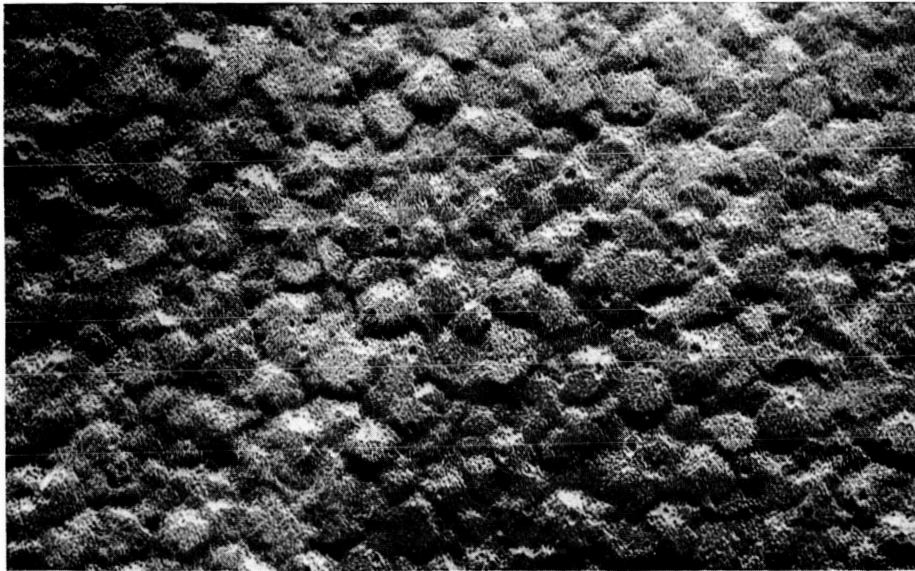


Fig. 2 Carbon replica of very nearly the same material as Fig. 1. Note fine resolution,
increased contrast and obvious nature of sample damage. (80,000 x)

III. THE CdS SURFACE

An electron microscopic investigation was performed on the surfaces of a series of CdS samples deposited at various substrate temperatures. In this way it was hoped to gain insight into the roles of the various deposition parameters in the formation of the structure of the deposit.

All samples in this investigation were deposited to a standard thickness of about 2625 \AA at a constant source temperature, the only controlled variable being the substrate temperature. When the surfaces were examined using the carbon replication technique described above, it was found that the results could be grouped into four basic categories.

A. UNHEATED SUBSTRATES (TYPE 1)

For these samples, the substrate temperature was allowed to drift with heat from the source, the average temperature being 22°C initially, drifting up to 28°C . The evaporation rate was essentially a constant during the entire deposition, averaging $400\text{-}500 \text{ \AA}/\text{min}$.

An example of this type of surface is shown in Fig. 3, where it is seen that it is composed of rounded lumps of extremely small grain size. They are less than 500 \AA across, and about 100 \AA in height above the average surface. This surface is characteristic of all samples deposited at substrate temperature up to about 80°C . There is seen no evidence of crystallinity, and no break in the general uniformity of the surface.

B. SUBSTRATES HEATED TO $82\text{-}96^\circ\text{C}$ (TYPE 2)

For this temperature range, the deposition rate is no longer a constant throughout deposition, but starts at an initially very high rate ($\sim 600 \text{ \AA}/\text{min}$.) and then "breaks" into lower rates as the amount of evaporable material in the boat decreases. The following graph shows a typical plot of thickness vs. time for this sample type, as well as a plot of the thermal drift during deposition. This figure is characteristic of any deposition performed at substrate temperatures higher than 80°C with a constant temperature, "degassed", molybdenum boat source.

Samples within this group show an extreme dependence on substrate temperature and evaporation rate. Figures 4-7 show surfaces deposited to the standard thickness of 2625 \AA at increasing substrate temperature.



Fig. 3 Type 1 surface, deposited on an unheated substrate. (80,000 x)

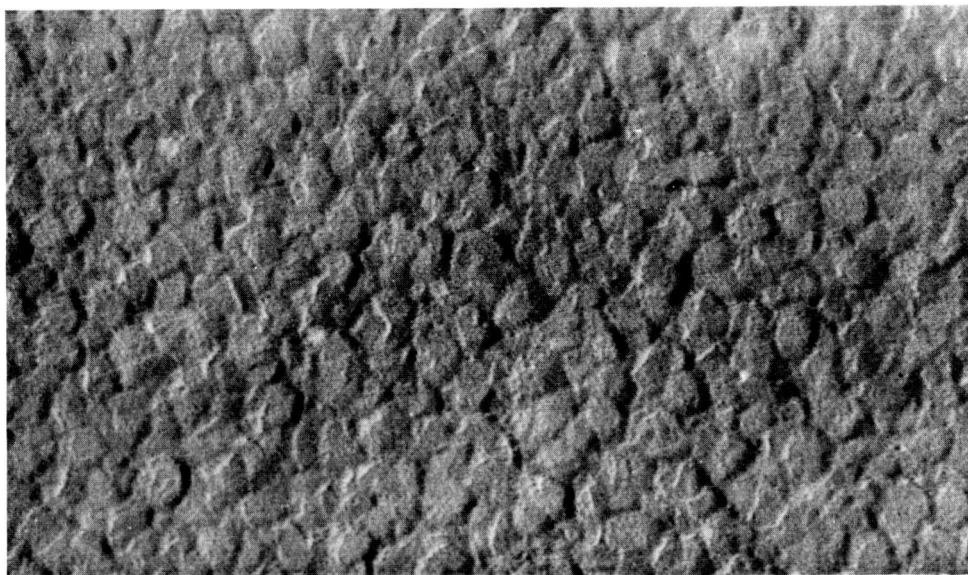
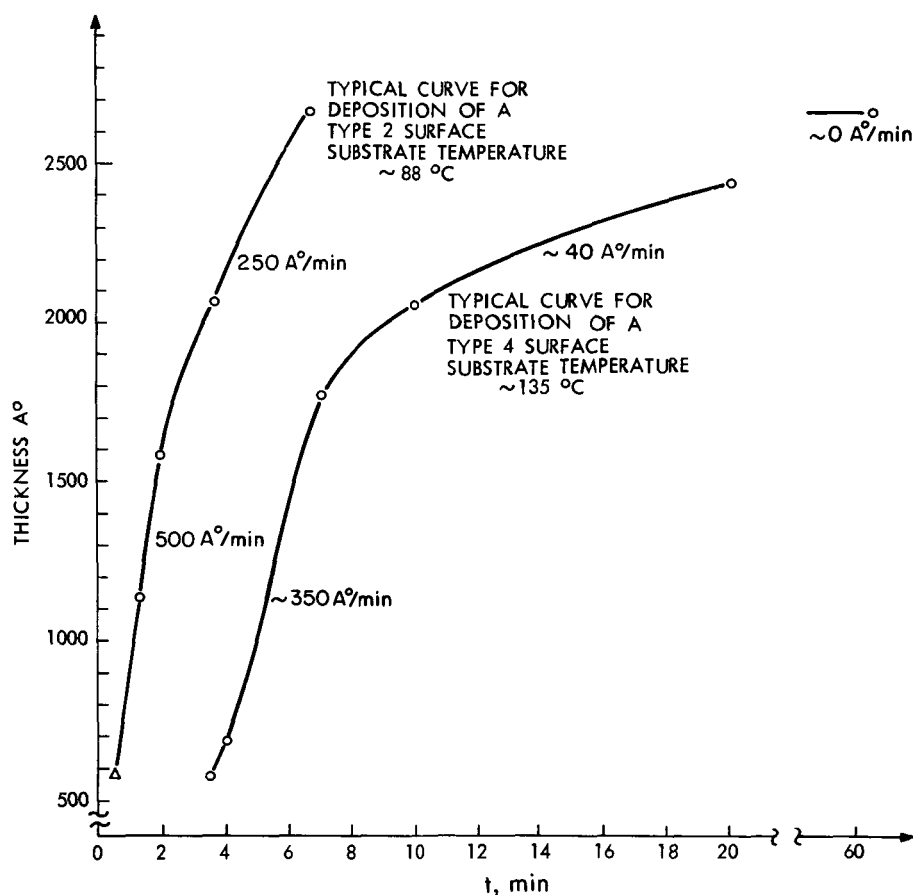


Fig. 4 Type 2 surface, substrate temperature 83-86°C. Grains are about 1000 Å in size and 100 Å high. (80,000 x)



Unlike Type 1 samples, once the substrate is exposed to the 885°C source, there is a time lag before the first visible deposition occurs. This time lag is a function of the substrate temperature, and is less than a minute at 82°C , extending up to 1.5 - 2 minutes at 93°C initial substrate temperature. The amount of material and the temperature of the source, however, are approximately constant for all samples, and hence the breakpoint of the deposition curve occurs at approximately the same time for all samples. The result is that the uppermost layers of samples grown at higher substrate temperatures are deposited at lower rates, even though their bottom layers are all deposited at essentially the same $600 \text{\AA}/\text{min}$. rate, due simply to the fact that it takes longer to reach the standard 2625\AA thickness with an exhausting source. For Fig. 4, only the top 600\AA were grown at a reduced rate, while

the top 1100 \AA of the sample in Fig. 7 were grown at a constantly reducing rate.

It is seen that the effect of this decay in deposition rate is to increase the size of the grains and to reduce the asperity of the surface. The nature of the surface is quite obviously crystalline for all samples of this type, and this crystallinity is thought to be due to the reduced deposition rate as the following argument suggests.

Consider a sparse layer of CdS which has just reached the substrate. Assume that the substrate is already covered with a film of condensed CdS. Presumably the molecules of this layer have some surface mobility at this elevated substrate temperature. They move around on the surface until they reach a spot where they become bound. Such a spot would most probably be in crystalline orientation with the underlying CdS surface. There is some characteristic lifetime for a mobile CdS molecule on such a surface--a "condensation time" for the layer. Now, if the source produces material at an extremely high rate, many more than one of these layers will be produced on the surface within the condensation time. This will mean that the very large number of mobile molecules will be forced to equilibrate--crystallize--with each other rather than with the underlying material. This process will be of a very local nature since the molecules do not have time to equilibrate over a large area--they are trapped by other material. This, coupled with the probable lack of mobility at low substrate temperatures, may explain the apparent lack of crystallinity and extremely small grain size of the Type 1 surface.

The reduction in rate and a higher surface mobility thus explain the crystallinity of the Type 2 surface. For Fig. 4 and 6, only the top $600 - 700 \text{ \AA}$ were deposited at a moderately slow rate. The grains are smaller and the asperity is higher than Figs. 6 and 7, where the top $900 - 1100 \text{ \AA}$ were deposited at a constantly reducing rate. For Figs. 6 and 7 the material has probably had time to equilibrate with the substrate, enlarging the grains and filling in the asperities. Experiments have shown that the Type 2 surface can only be produced at the $82 - 96^\circ\text{C}$ substrate temperatures indicated--they cannot be made with a low rate on a cool substrate. This supports the reasoning that the elevated substrate temperature produces the required mobility.

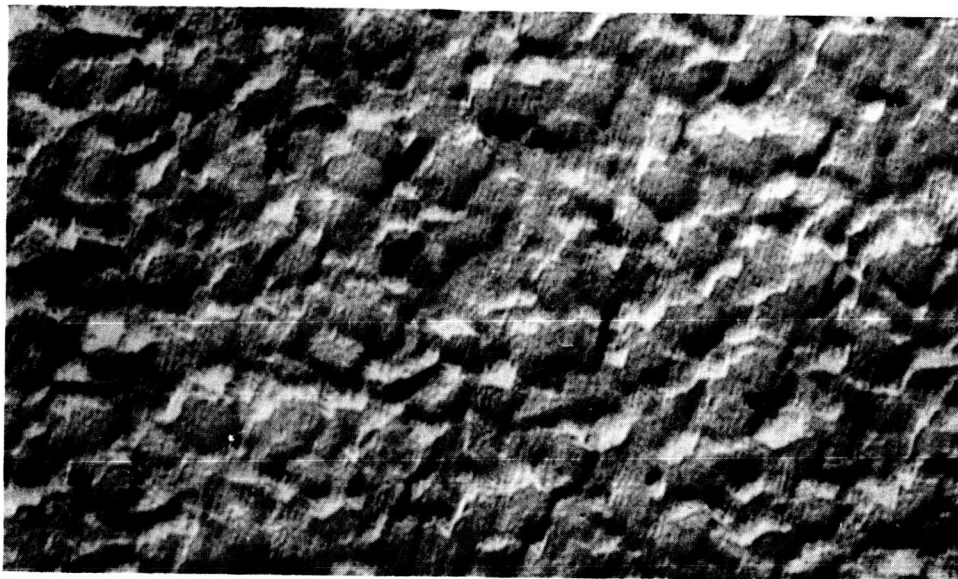


Fig. 5 Type 2 surface, substrate temperature 87-90°C. Grains are about 1000 Å in size and about 100 Å high, but boundaries are more diffuse than in Fig. 4. (80,000 x)

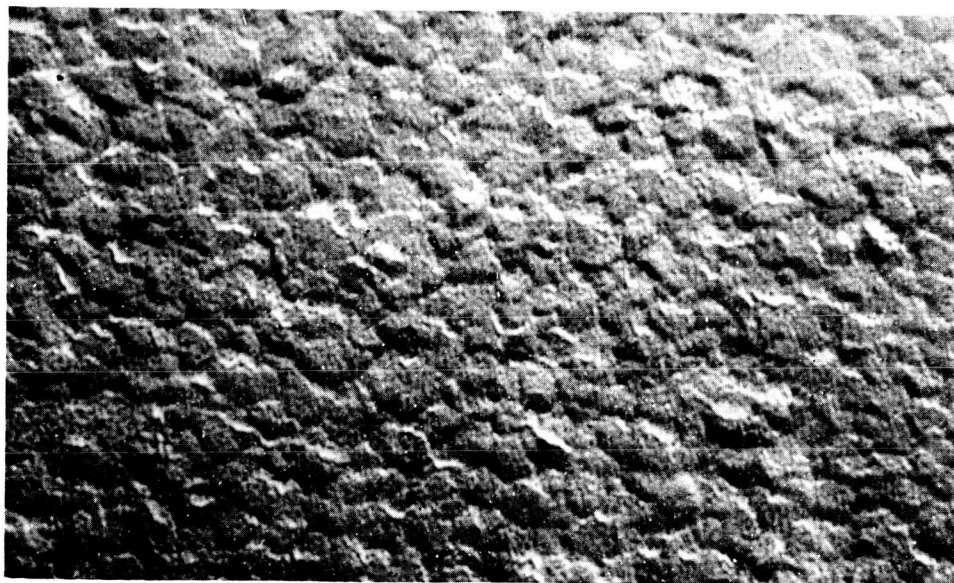


Fig. 6 Type 2 surface, substrate temperature 88-93°C. Grains are about 1000 Å in size and 50-75 Å in height. (80,000 x)



Fig. 7 Type 2 surface, substrate temperature $93-96^{\circ}\text{C}$. Grains are about 1750 \AA in size and 75 \AA in height. (80,000 x)

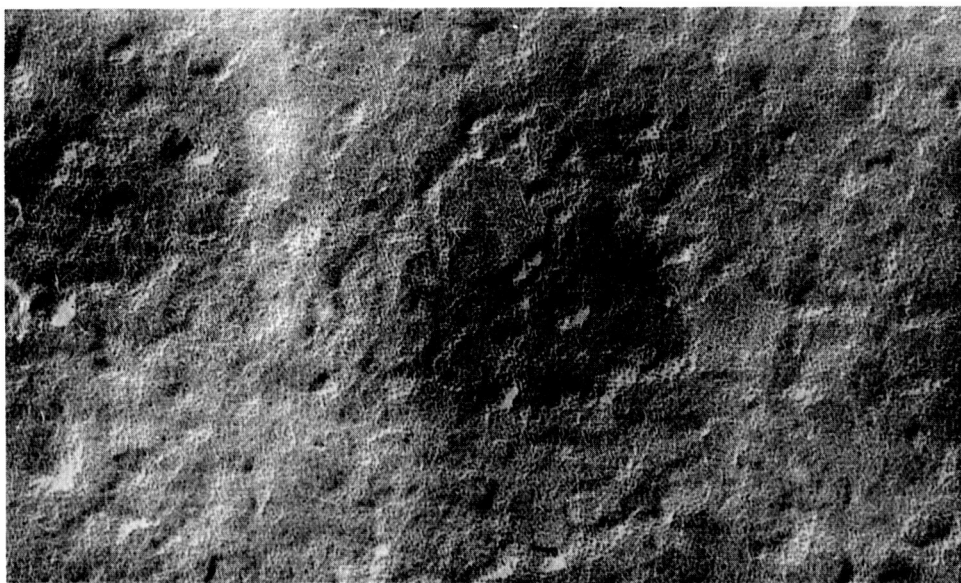


Fig. 8 Type 3 surface, substrate temperature $123-126.5^{\circ}\text{C}$. Note 2500 \AA grains surrounded by narrow troughs $3-400\text{ \AA}$ wide and 150 \AA deep. (80,000 x)

C. SUBSTRATE TEMPERATURES 110°-130°C (TYPE 3)

There was found to be no fundamental difference from Type 2 in deposition process for samples of this type. Since the initial substrate temperature was higher, the time lag from hot source to first deposition was longer, as expected. The break point in deposition rate was found to occur after correspondingly less material had been deposited, and grain size and surface smoothness increased.

Figure 8 shows a surface produced at this temperature. The time lag was so long for this sample that the deposition rate for the source had already begun to decay. The initial rate was about 500 Å/min. and this rate slowly decreased until, at the end of two hours, when the standard thickness had been deposited, it was under 5 Å/min. (This was measured as the average rate from 60 to 120 minutes deposition time.) This rate is apparently slow enough to allow the growth of the large single crystals seen in the plate. The presence of these and the extreme smoothness of the surface are the characteristics of this type of material.

D. SUBSTRATE TEMPERATURES ABOVE 130°C (TYPE 4)

The initial deposition rate for this material was under 400 Å/min. which decayed to something immeasurably small after 40 minutes. Samples in this temperature range have no well-defined thickness. The high temperature of the heater produces a heat flow across the substrate which does not come into equilibrium for any reasonable length of time. The result is that the substrate has a thermal distribution across it, and since deposition rate is a sensitive function of substrate temperature, there is always a distribution of thicknesses on the substrate during deposition. This the rate of deposition cannot be measured easily from the color of the substrate--it can only be estimated. The substrates were exposed to the source for about 60 minutes, during the last 20 of which there was no visible deposition.

Figure 9 is an example of this surface. It was hoped, following the reasoning of the last two sections, that it would consist of even larger crystals than the Type 3 surface, and that these would be closer together. If this does occur, it is not evident from the figure. There are no well-defined grains, and there is nothing which is obviously crystalline. The surface is very smooth, however, and may well serve as an excellent substrate for field effect "grid" depositions in device work.

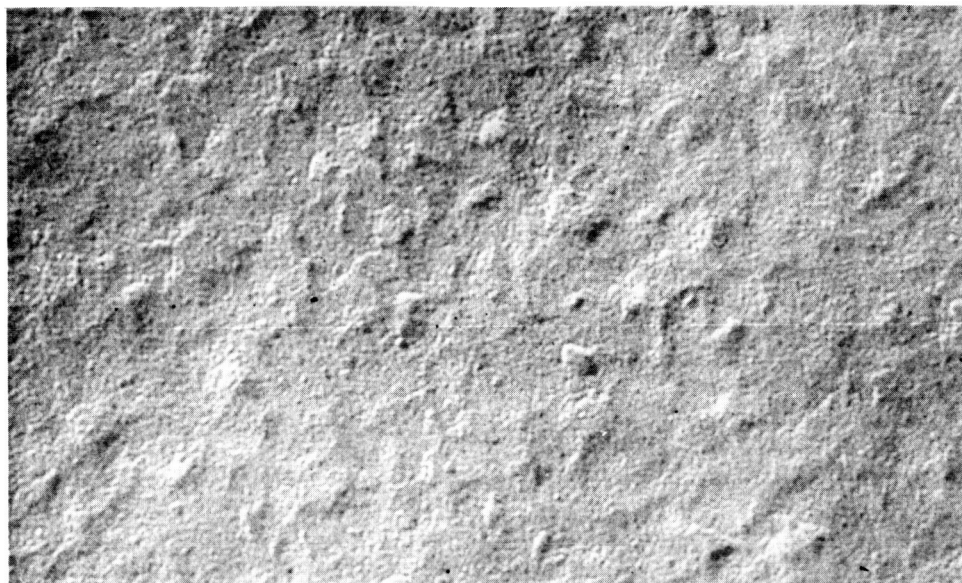


Fig. 9 Type 4 surface, substrate temperature $130-133^{\circ}\text{C}$. There are no well-defined grains and the surface is very smooth. (80,000 x)

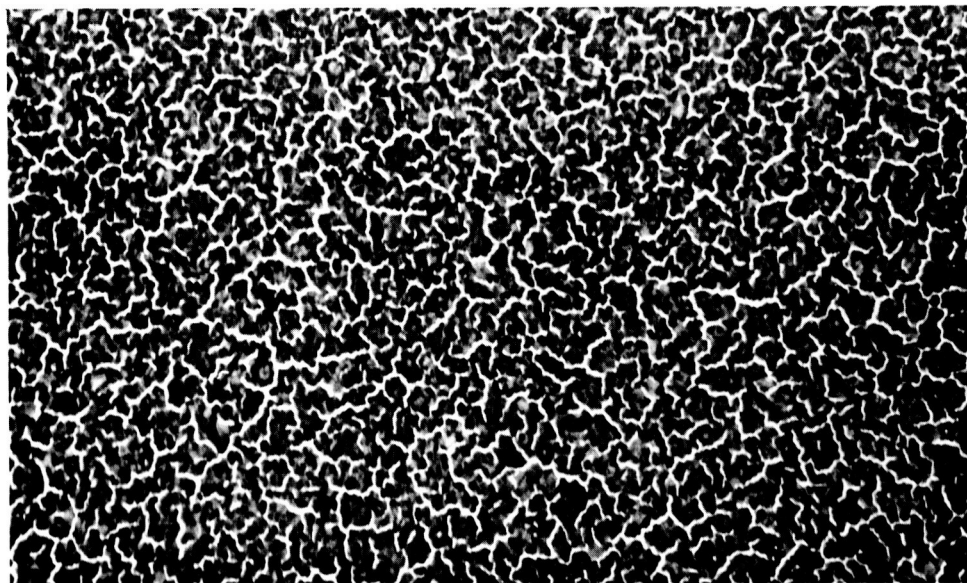


Fig. 10 $15\text{ }\mu\text{g}/\text{cm}^2$ of Au deposited on unheated glass. Open channels are $30\text{ }\text{\AA}$ wide, nominal thickness is about $100\text{ }\text{\AA}$. (80,000 x)

E. DISCUSSION

It was stated in the arguments given above that the occurrence of the break in deposition rate at a variable thickness was due to a variation of the lag time with substrate temperature. It is also possible that an elevated substrate temperature can suppress the deposition rate even before the source becomes exhausted, by causing the re-evaporation of mobile material from the substrate. Probably, re-evaporated material will not return to the substrate--it will deposit on the cold parts of the evaporator. Hence, to reach a given thickness, the source must evaporate more material than it would to reach the same thickness at a lower substrate temperature. This means then, that the source will become exhausted at an even lower deposited thickness than that prescribed by the long lag time. This effect gives additional reasons why the deposition rate for the Type 3 and 4 samples is suppressed even in the initial stages of the evaporation.

The boat source is peculiar in that it can produce the breaks in deposition rate described above. It has yet to be determined whether this break is necessary for the production of crystalline surfaces, or if a uniform but low rate will produce a similar surface at the same substrate temperature. A uniformly high rate at high substrate temperatures cannot be studied with this source, so it is not known whether these conditions produce structures which can be explained with the above argument.

The presence of a bluish scale on the used molybdenum boat is evidence that CdS reacts chemically with the source. This could give rise to two effects: First, there may be an evaporation of MoS as an impurity; and second, this reaction, by absorbing sulfur from the evaporant, could enhance the evaporation of sulfur deficient material, in turn causing sulfur vacancy in the deposit. (These effects are further discussed in the section on diffraction analysis.)

It is evident that there is much work to be done with an inexhaustible, non-reacting source which could cause impurities and stoichiometric changes in the evaporant only through thermal decomposition which (hopefully) would be negligible. This source, coupled with some accurate method of determining deposit thickness,* could produce important data on the relationship between surface crystallinity, deposition rate, and substrate temperature.

* Such an accurate deposition rate sensor is described in the third quarterly progress report, "Metal Base Transistor", Philco Research Laboratories, Signal Corps contract No. DA-36-039-AMC-02373(E) (Jan. 1 to March 31, 1964). Since it is essentially a crystal controlled oscillator, however, it cannot be used at elevated substrate temperatures.

The nature and causes of the lag time are not well understood. It is only known that it is longer for higher substrate temperatures. It may well be affected by the cleanliness of the substrate, the pressure in the evaporator, and the amount of light shining on the substrate. (It has been noted in some experiments that the deposition rate for CdS is slightly photosensitive--the brighter the substrate, the higher the rate.)

The electrical characteristics of the materials represented by the various surface types have yet to be determined. Before this work can proceed in any well-defined way, the metal-CdS surface interaction should be studied from the point of view of electrical contact to the material. This is the topic of the second phase of this work.

IV. DEPOSITION OF GOLD ON CdS SUBSTRATES

It was found that gold structures deposited on CdS substrates are very different from those deposited on glass under the same conditions. (See Figs. 10 and 11). The lacy network of open channels of the gold deposited on glass had been thought to lend itself ideally to field-effect device work, but, as is evident from the plates, Gold on CdS presents an essentially solid layer. It became necessary to study the nature of the Gold-CdS surface interaction--to look for the causes of the "solid-layer" effect, and to see if these causes could be manipulated through the deposition parameters.

A. $2.74 \mu\text{g}/\text{cm}^2$ GOLD ON CdS

The study was begun by examining the structure of a $2.74 \mu\text{g}/\text{cm}^2$ surface density of gold as it varied with substrate temperature and post-deposition thermal cycling. The nominal thickness of this amount of material is less than 15 \AA , and it was thought that if a regular pattern of active nucleation sites were present on the CdS surface, they would be clearly revealed through "decoration" by the very thin gold film. (Decoration refers to a preferential build-up of material at active sites.)

The first experiments were done with the CdS substrate at room temperature. Figures 12, 13, and 14 are examples of the results. Note that the structure is a very uniform distribution of extremely small grains, narrowly spaced, apparently without regard to the underlying CdS structure. The grain size is plainly larger on Type 4 CdS than on Type 2, though the spacing remains the same. The number of grains per unit area is thus reduced on Type 4, and these facts are sufficient to show that there is a difference in the magnitude of the adhesive force between the gold and the CdS on the Types 2 and 4 surface. Consider first the Type 2 surface (Fig. 12). The grains seen here are agglomerates of, at most, a few hundred atoms. Presumably, these are formed either through a nucleation of individual atoms on the surface which were deposited so close together that they were pulled into the grains seen here, or through nucleation by collisions of mobile atoms on the surface. These grains rarely further coalesce on the Type 2 surface, as is seen from a careful examination of Fig. 12. The Type 4 surface, on the other hand, exhibits many instances of coalescence of the nuclei--the average grain size, in fact, is doubled. This can only mean that the grains themselves must have some local

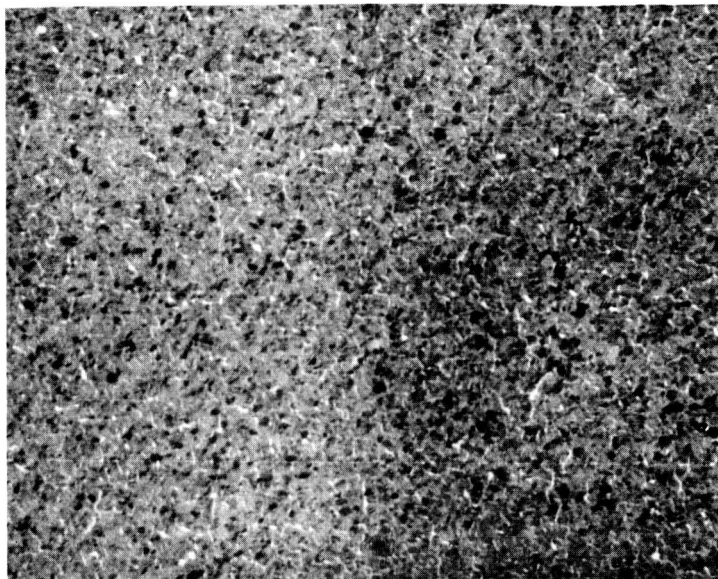


Fig. 11 $15 \mu\text{g}/\text{cm}^2$ of Au deposited on unheated Type 1 CdS. Structure is referred to as a "solid layer". (80,000 x)



Fig. 12 $2.74 \mu\text{g}/\text{cm}^2$ Au deposited on Type 2 CdS at 30°C , 60 sec. deposition time. Gold grains are 25 \AA in size, spacing is 25 \AA or less. A "combination" specimen. (80,000 x)



Fig. 13 $2.74 \mu\text{g}/\text{cm}^2$ Au on Type 4 CdS, same deposition conditions as Fig. 12. Size is 50 \AA and spacing is 25 \AA . Combination specimen. (80,000 x)

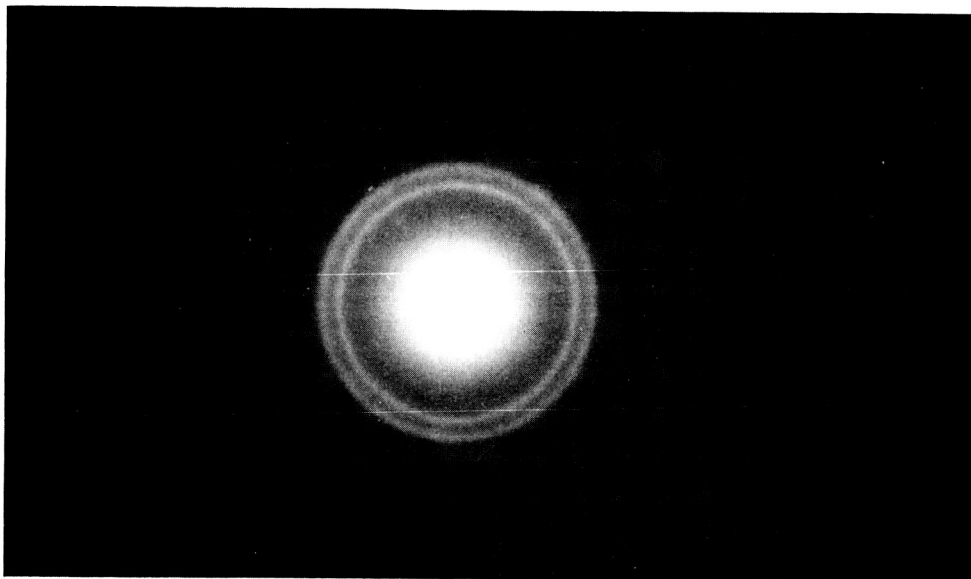


Fig. 14 Transmission electron diffraction pattern characteristic of the material of Figs. 12 and 13. Diffuse rings due to small grain size.

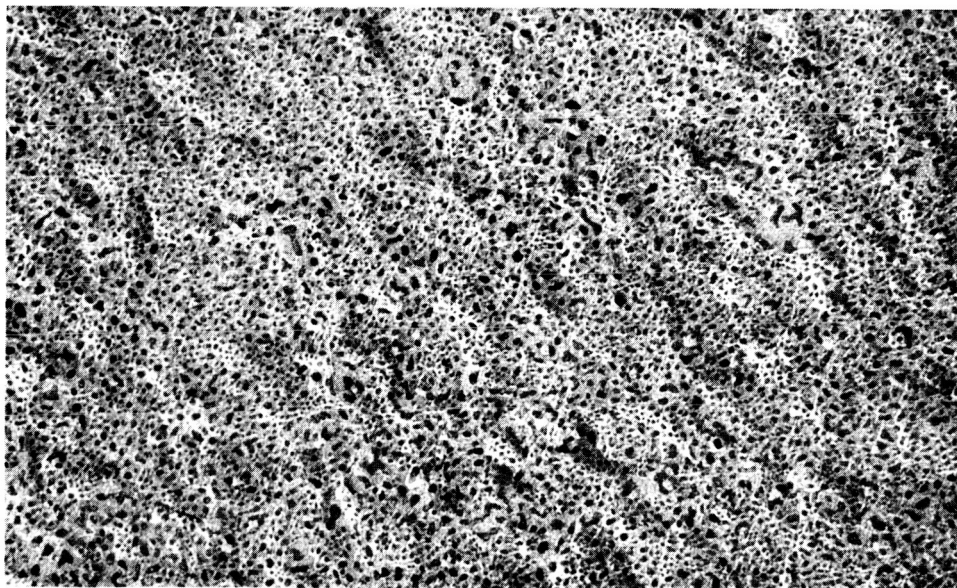


Fig. 15 $2.74 \mu\text{g}/\text{cm}^2$ Au on Type 2 CdS at 30°C , 52 sec. deposition time. Past deposition anneal at 105°C for 90 min. Size is 150 Å and spacing is 100 Å. Note examples of coalescence. Combination specimen. (80,000 x)

surface mobility on Type 4 CdS, and that this mobility is sufficient to enable the cohesive force between gold nuclei to exceed the adhesive force from the surface. This condition produces the coalescence, and since it apparently cannot occur on the Type 2 surface, the surface adhesion for gold must be greater on Type 2 than on Type 4 CdS.

The effects of a post-deposition "anneal" of 100°C for 70 minutes on this mechanism were then examined, and Figs. 15, 16, and 17 show the results. Remembering that the same mass density as on Figs. 12, 13, and 14 was deposited here, it is seen that the thermal cycling had a large effect on the surface adhesion, especially on the Type 2 surface. The gold grain size is increased, but most noticeably on top of the grains of CdS seen shadowed in the background, where there are some examples of double and triple coalescence of the already enlarged gold grains. On the surface between the CdS grains this does not appear to happen, and in fact, in some of these locations, gold grain size and separation are not very different from the unannealed case.

The structure on the Type 4 CdS surface, when compared with the structure of the unannealed case (Fig. 13) shows that the effect of annealing is again to reduce the surface adhesion, and thus to produce these larger, more widely separated grains. Comparing Fig. 16 and 17, it is seen that annealing the gold deposit on a Type 4 surface produces none of the large local coalescences and a much smaller range of grain sizes than it does on Type 2. From this it might be concluded that the Type 4 CdS surface presents a more uniform substrate (with respect to active nucleation sites) for gold deposition, and that the effect of temperature on its adhesiveness is ~~neither~~ as strong as it is on top of the Type 2 CdS grains, nor as weak as it is on the material between the Type 2 grains.

In any event, it is evident that the adhesion of the gold-CdS interface is reduced as temperature is increased, and that the consequent grain coalescence mechanism can maintain spaces between the grains, possibly solving the "solid-layer" problem.

The effect of heating the substrate during gold deposition was checked and compared with the effect of post-deposition heating. Figure 18 shows a result for an extreme case on Type 2 CdS. Here the deposition substrate temperature was almost 3 times the "anneal" temperature of the previous samples (Figs. 15, 16, and 17), and it is obvious that the effect is not as pronounced. Compared with Fig. 15 (annealed gold on a Type 2 surface), none of the large

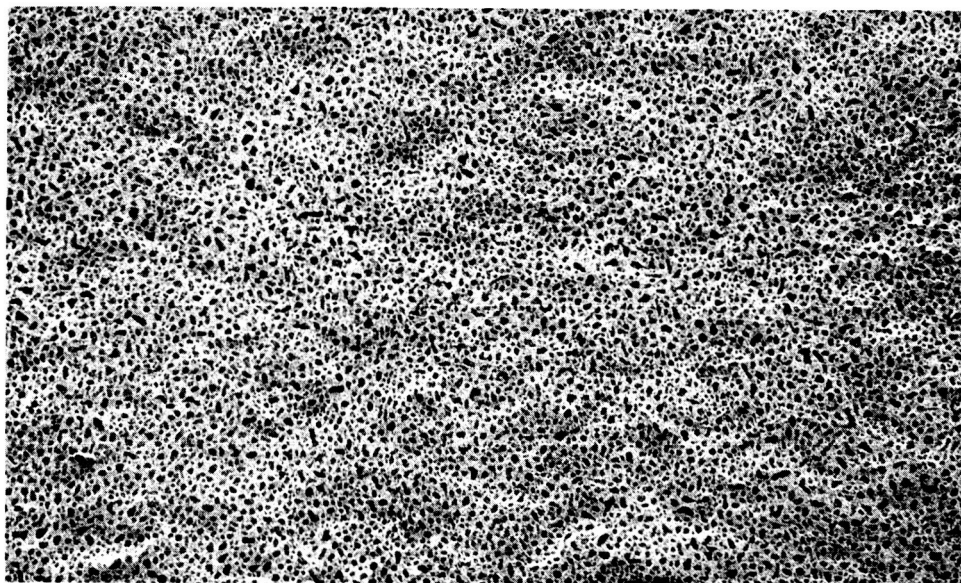


Fig. 16 $2.74 \mu\text{g}/\text{cm}^2$ Au on Type 4 CdS, same deposition conditions as Fig. 15. Size is about 100 \AA , spacing is 200 \AA . Combination specimen. (80,000 x)

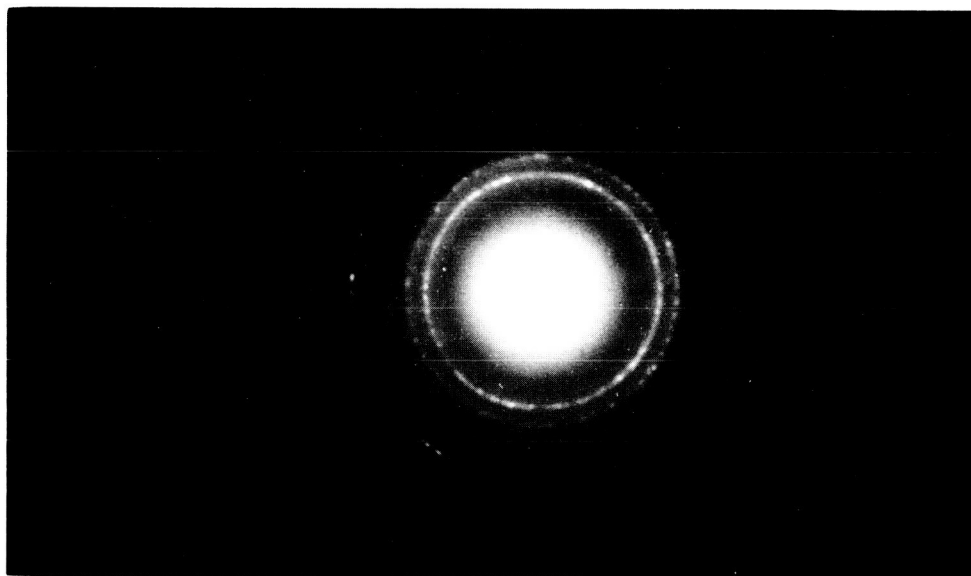


Fig. 17 Diffraction pattern characteristic of the material of Figs. 15 and 16. Note the sharper rings and "preferential" marks on (220) ring. Indicative of increased crystallinity.

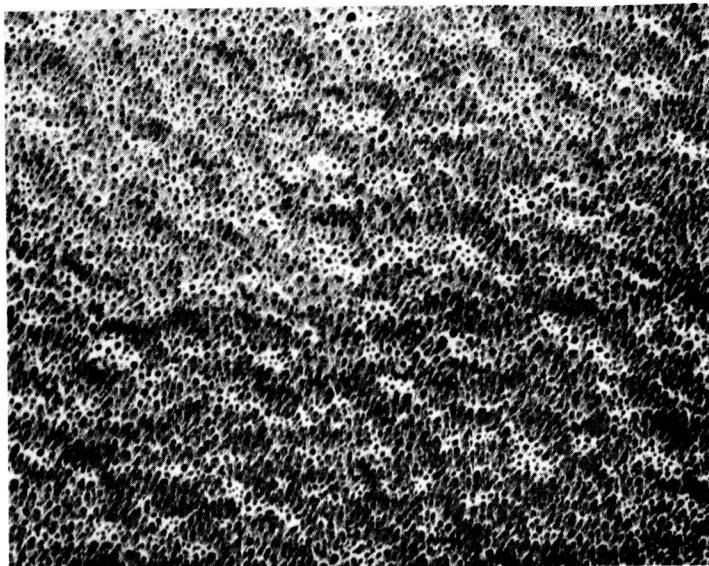


Fig. 18 $2.74 \mu\text{g}/\text{cm}^2$ Au on Type 2 CdS at 290°C , 56 sec. deposition time. Size is 100 \AA spacing 200 \AA . Combination specimen. (80,000 x)

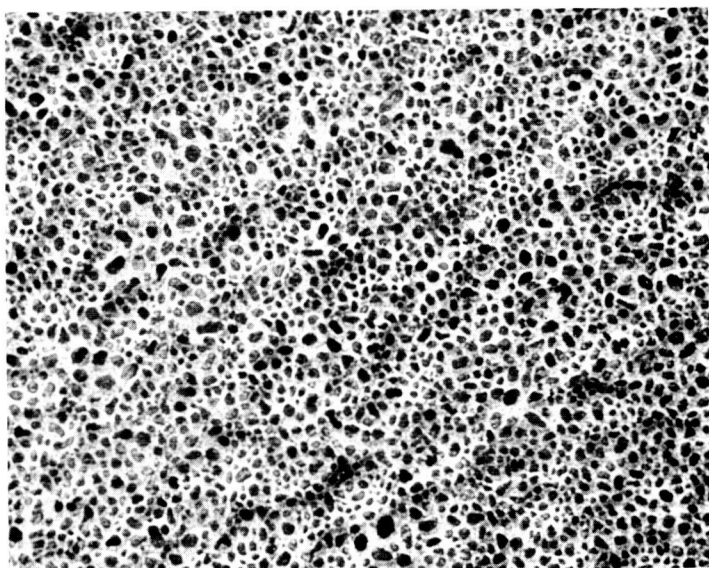


Fig. 19 $5.48 \mu\text{g}/\text{cm}^2$ Au on Type 2 CdS at 205°C , 105 sec. deposition time. Size is $250\text{--}300 \text{ \AA}$ average, spacing is $125\text{--}150 \text{ \AA}$. Combination specimen. (80,000 x)

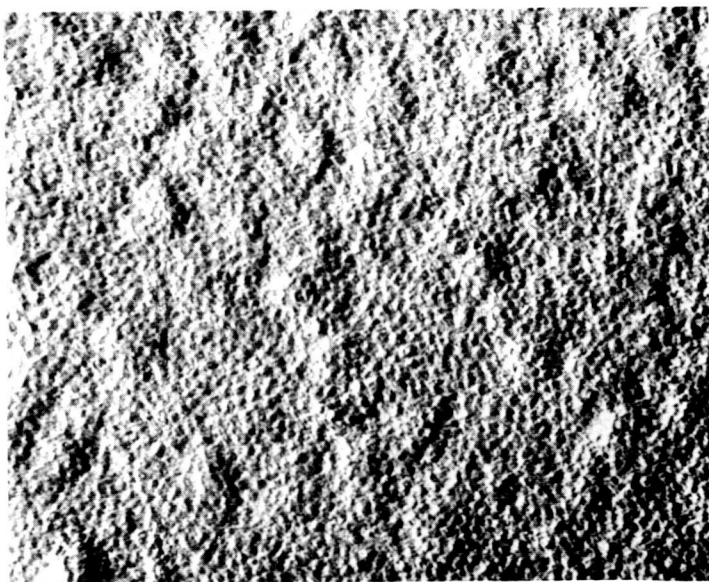


Fig. 20 Simple replica of material of Fig. 19. Thickness of grains is 25 \AA . Note high resolution (80,000 x)

coalescences are seen, and the over-all gold grain size is reduced and more uniform.

Doubtless, this is due to the fact that coalescence cannot occur until the grains are of full size and are almost touching, especially on a Type 2 surface, and even then it occurs only over a long period of time. Remember that the post-deposition anneals were 90 minutes long, while here the substrate was cooled immediately upon completion of deposition.

It must then be concluded that an increased substrate temperature during deposition, while it has some effect, is not nearly as effective as post-deposition annealing in producing coalescence.

B. HIGHER SURFACE MASS DENSITIES

A preliminary study was then undertaken to check whether the coalescence mechanism still works for increased amounts of deposited material.

Figure 19 shows that when $5.48 \mu\text{g}/\text{cm}^2$ of gold are deposited at an elevated substrate temperature of 200°C , the gold grains apparently reach the size necessary for coalescence before deposition is complete, and the structure exhibits large grain size and high separation, even without resort to the annealing process. It was assumed that coalescence could not occur unless the deposition substrate temperature was elevated, no matter what grain size is reached during deposition, since this seems to be precisely what occurs in the "solid layer" effect of Fig. 10.

Figure 21 shows $8.23 \mu\text{g}/\text{cm}^2$ of gold deposited at 287°C substrate temperature. This material was deposited very slowly to enhance the effect of the temperature on the coalescence during deposition, thereby maintaining a grained structure as the finished product.

The next step in this work is to apply the annealing technique to the structures of Figs. 19 and 21 and determine whether further coalescence can be made to occur. It is fairly certain that it can, and ~~that~~ the result will be larger, thicker grains, more widely separated than before. It is thought that the same technique applied to surface mass densities up to about $15 \mu\text{g}/\text{cm}^2$ will still produce the grained structure, and that densities higher than this will form the solid layer.

Work has yet to be done with the application of annealing to an initially "solid layer," but if present indications are true, the fine openings in this structure may be enlarged. Currently it is thought that more desirable proper-

ties of the gold structure can be obtained by annealing an initially grainy structure than by trying to make a solid layer grainy with annealing.

Another technique, which could be very useful, is that of applying a voltage across the gold deposit during the annealing process. It is clear that the electrostatic force applied to the grains will enhance the coalescence mechanism and perhaps so increase the cohesion between gold grains that little "bridges" of gold will form between them, producing the "gridlike" structure desirable in applications to field effect device work.

No mention has been made in the above discussion of the possibility that diffusion of gold into the CdS can occur. Clearly, this could occur, and if it does, it would almost certainly be a function of substrate temperature. Careful checks have shown that the extreme thermal cycling to which the substrate is subjected has no apparent effect on the CdS surface, but this in no way precludes the possibility that these temperatures increase (or decrease) its susceptibility to gold diffusion. Work is obviously needed in this area.

Another measurement which would be of considerable interest is the correlation between the grainy, non-adhered character of a gold deposit and the nature of the contact it makes with the CdS surface. Two possibilities come to mind immediately: First, that a grainy deposit, simply because it makes poor contact with the surface, will not inject electrons, while an adhered deposit might be in good electrical contact. Second, if an adhered deposit is partly diffused into the CdS surface, it might act as an acceptor impurity at the surface and form a p-type layer in the CdS. This would provide an essentially blocking contact. The results of this correlation must be known before the techniques discussed above can be used in any well organized way in the fabrication of field-effect devices.

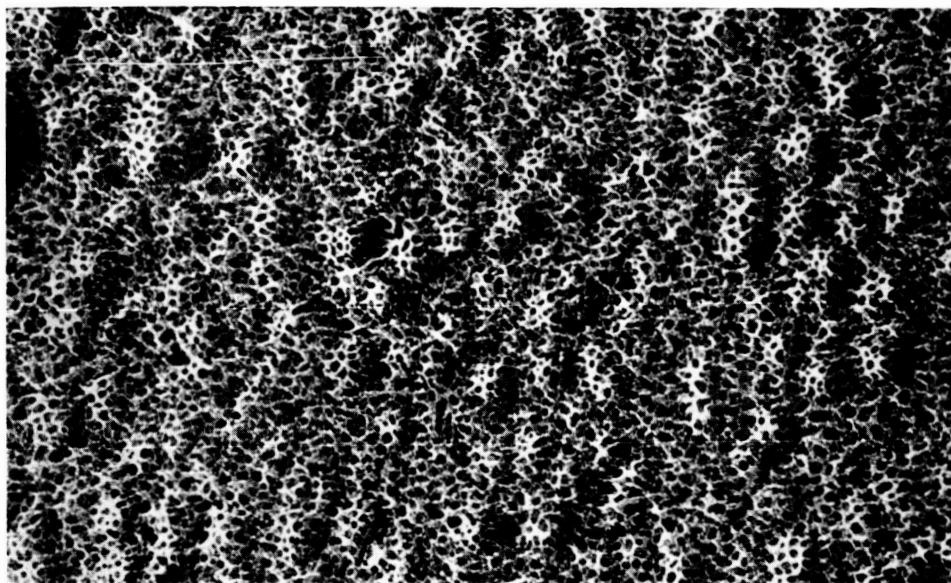


Fig. 21 $8.23 \mu\text{g}/\text{cm}^2$ Au on Type 2 CdS at 287°C , 30 min. deposition time. Size is 250-300 Å, and separation is 50-100 Å. Combination specimen. (80,000 x)

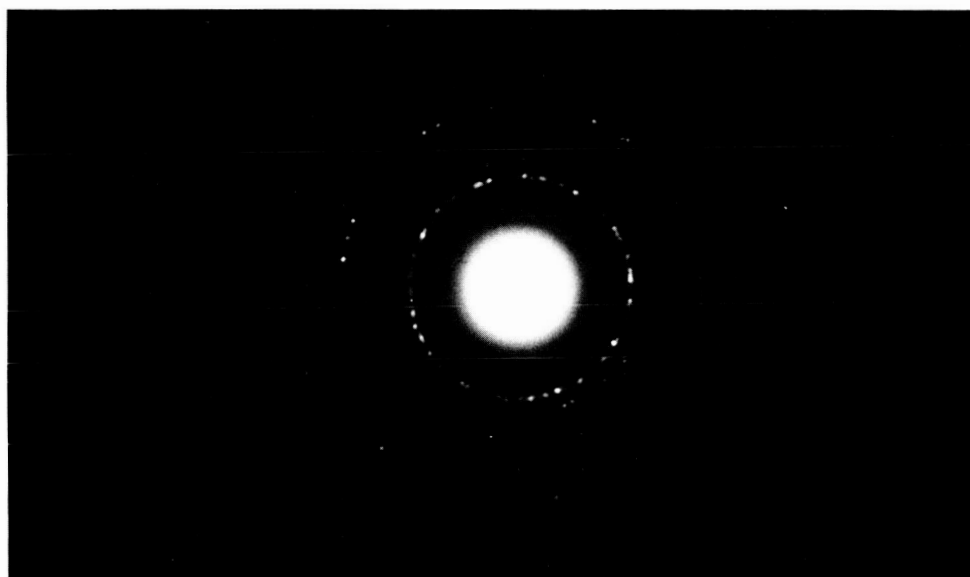


Fig. 22 Diffraction pattern for the material of Fig. 21, characteristic of all higher surface mass densities on hot substrates. Note "beads" due to crystallinity of grains.

V. DIFFRACTION ANALYSIS OF CdS SURFACES

An electron diffraction analysis of the Types 2, 3, and 4 CdS surface was performed and some interesting results were noted.

Figure 23 shows a transmission electron diffraction pattern from a CdS sample which was deposited directly on an unheated microscope grid covered with a film of Parlodion. The deposited layer was about 500 Å thick on the glass support surrounding the grid. It was found that under these conditions there was a thin layer of CdS on the grid which produces the full powder pattern for CdS. Thicker layers were opaque to the electron beam. The data of Fig. 22 is presented in the following table:

<u>Ring</u>	<u>Spacing</u>	<u>Orientation</u>	<u>ASTM Spacing</u> ¹
1	3.583 Å	(100)	3.583 Å
2	3.071	(101)	3.160
3	2.419	(102)	2.417
4	2.047	(110)	2.068
5	1.887	(103)	1.898
6	1.728	(201)	1.731
7	1.594	(202)	1.581
8	1.387	(203)	1.398

Rings are numbered with lower numbers toward the center. The first ring was used to calibrate the rest. An accurate determination of sizes was not desired, since it was hoped to find missing rings and thereby determine the crystalline orientation at the surface. Rings missing in Fig. 23 are the (002) which is probably hidden by the relatively high intensities of the (100) and (101), the (200) and (112), which have probably been lumped with the (201), and the (004) and (104) which are seen, but are too faint to measure.

Figure 24 is the diffraction pattern characteristic of the Types 2, 3, and 4 surfaces. The sample for this pattern was prepared by incompletely removing the CdS from a carbon replica made in the standard way. The material which remains on the replica is that which is in crevices -- the surface

¹ "X-Ray Powder Data File," ASTM publication 48L, as quoted in C. A. Escoffery, J. Appl. Phys., 35, 2273 (1964).

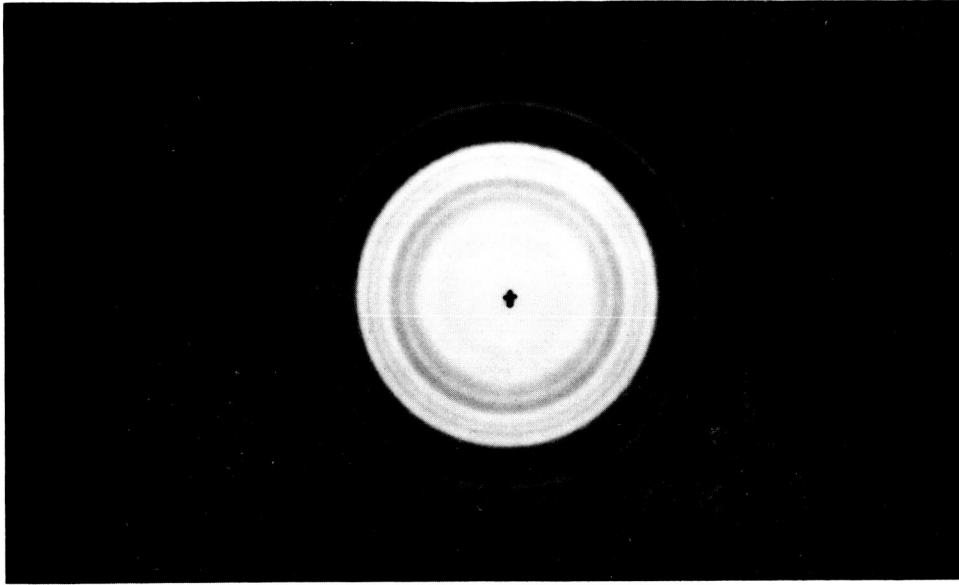


Fig. 23 CdS powder pattern by electron transmission diffraction.

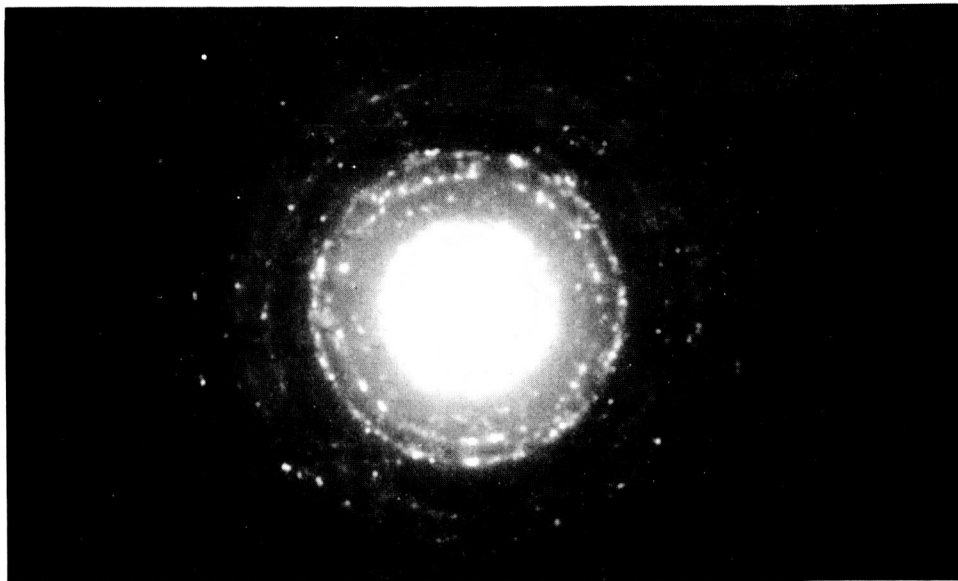


Fig. 24 Transmission diffraction pattern from surface material. Characteristic of Types 2, 3 and 4.

material of the deposit. Checks were made to see that the carbon replicating material was amorphous enough not to interfere with the pattern from the CdS, with very satisfactory results.

Data from Fig. 24

<u>Ring</u>	<u>Spacing</u>	<u>Orientation</u>	<u>ASTM Spacing</u> ¹
1	3.613 Å	(100)	3.583 Å
2	3.357	(002)	3.357
3	3.150	(101)	3.160
4	2.559	(102)	2.450
5	2.048	(110)	2.068
6	1.862	(103)	1.898
7	1.781	(200)	1.791
8	1.706	(112)	1.761
9	1.575	(202)	1.581
10	1.365	(203)	1.398
11	1.280	(114)	1.308

The pattern was calibrated with the ASTM data in an average over all rings. It is seen from the pattern that the residual material is quite crystalline, implying that the original surface itself was of a crystalline nature. It must be noted that there are no rings missing in the data which are not missing on Fig. 23, and in fact, due to the "beaded" nature of the rings, more of them could be measured than on Fig. 23. If the material were oriented perfectly with its c-axis normal to the substrate, none of the diffractions with a c-component should be seen, or if they are seen, they should be very faint. (This work was done by transmission.) This is not the case here, and this fact stands in agreement with results from other work,* where a high degree of preferred orientation is not to be expected until the sample thickness is about 1 micron. The samples here were only 2,000 Å thick.

In the course of the above work, a singular pattern was often noted and recorded. An example of this pattern is shown in Fig. 25, and the chunk of material which produced it is shown in Fig. 26. The lattice spacings represented by the dots can be very accurately calibrated against the gold powder

* Most notably that of R. Addis, Jr., Transactions of the Tenth National Vacuum Symposium, p. 354 (Macmillan, 1963).

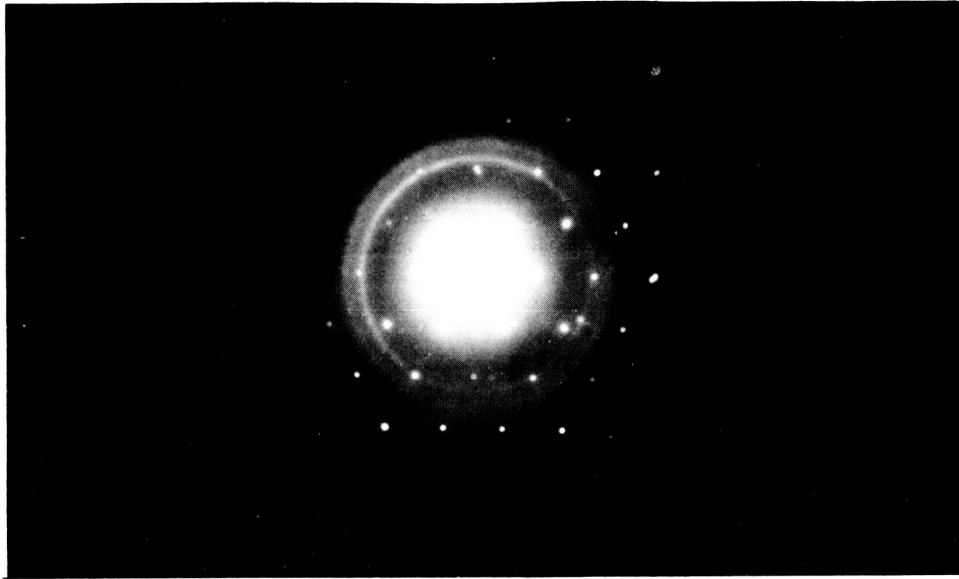


Fig. 25 Singular hexagonal Bragg pattern, by electron transmission diffraction.

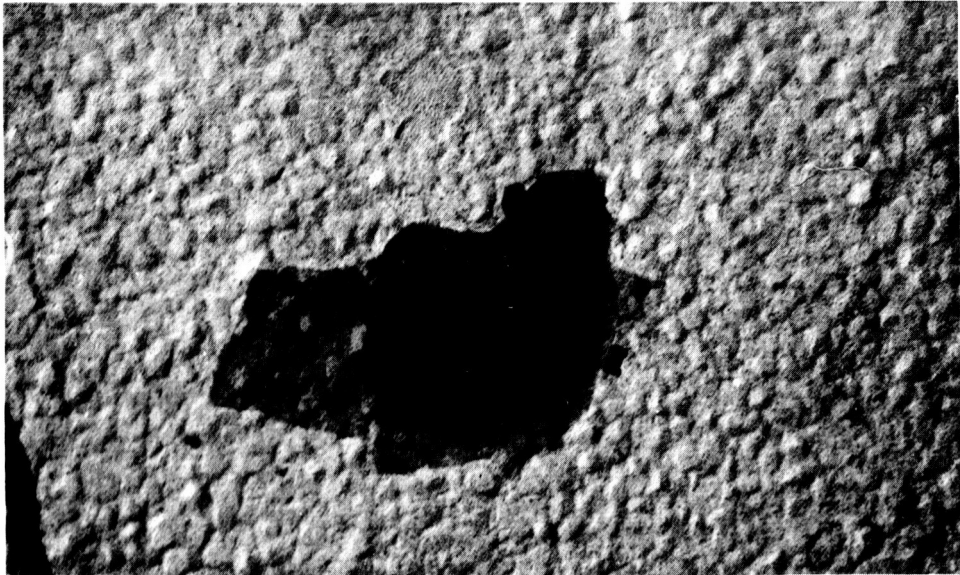


Fig. 26 The selected area which produced the pattern of Fig. 25.

pattern superimposed on it. The gold pattern is due to a $2.74 \mu\text{g}/\text{cm}^2$ layer which remained on the carbon replica. The chromium used to shadow the replica was found to produce no diffraction pattern. The data presented in the following table represents an average of results from 8 different measurements all of which were calibrated against superimposed gold rings:

<u>D</u>	<u>Spacing</u>	<u>Orientation</u>	<u>Cell Edge (A)</u>
1	4.5356 Å	(100)	5.237 Å
2	2.6052	(110)	5.290
3	2.2633	(200)	5.227
4	1.7287	(210)	5.281
5	1.5282	(300)	5.293
6	1.3201	(310)	5.280

"D" refers to the distance of each spot from the center, numbered from lowest to highest. It is seen from the data that the material is strictly hexagonal and is oriented with its c-axis normal to the substrate. No patterns for this substance have ever been recognized with any c-component diffractions.

A careful check of published tables was made to determine what this substance might be.* A list of possibilities which were definitely not this structure follows:

<u>Substance</u>	<u>Reason Disqualified</u>
Cd	Cell Edge too small
Cd-Au, α_1	Cubic
Cd-Au, α_2	Cell edge too small
Cd-Au, α_3	Cell edge too large
Cd-Au, β	Cubic
Cd-Au, β'	Orthorhombic
CdCl ₂	Cell edge too large
CdO	Cubic
CdS, α	Cell edge too small
CdS, β	Cubic
C (graphite)	Cell edge too small

* Principally, "Crystal Data," Donnay and Nowacki, Geological Society of America; Memoir 60 (1954).

<u>Substance</u>	<u>Reason Disqualified</u>
C-Cr	Cell edge too large
C-O-S	Cell edge too large
C-Ta	Cubic
Cr (hex. form)	Cell edge too small
CrC	Cubic or orthorhombic
Cr ₂ O ₃	Cell edge too small
Mo	Cubic
Mo-O compounds	None hexagonal
MoS ₂	Cell edge too small
Ta	Cubic
TaC	Cell edge too small
TaS	Cell edge too small

Any substance which had the correct hexagonal cell edge was composed of elements not found in any process leading to the finished specimen.

It is presently thought that this unknown material might be a form of cadmium oxide peculiar to thin-film layers. The mechanism for its production could be explained by remembering that molybdenum boats could deposit sulfur-deficient CdS, which may have oxygen in the sulfur vacancies (especially near the surface of the deposit) upon subsequent exposure to the air.* It is not known whether the presence of sulfur or gold is required to form this substance, but more can easily be learned from a careful diffraction analysis of appropriately made specimens.

* This argument is strengthened by observing that a layer of deposited cadmium (hexagonal), when oxidized on the substrate, has a distinctly hexagonal macrostructure. See Vacuum Deposition of Thin Films, Holland; (J. Wiley and Sons, 1961) Fig. 24a.